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Short communication

Light emission during electric field-assisted sintering of electroceramics

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Abstract

Electric field-assisted sintering has been shown to occur in ion, electron conducting as well as in insulating polycrystalline ceramics. Considerable linear shrinkage with microstructure control at temperatures lower than the conventionally utilized has been attained mainly in oxide ion conducting zirconia-based solid electrolytes. Some mechanisms, based on localized Joule heating and enhancement of defects diffusion, have been set forth to explain the sudden volume reduction in those ceramics. The results here reported contribute to the understanding of what happens *during* electric field-assisted sintering, by evidencing the occurrence of light emission simultaneously to the quasi instantaneous specimen shrinkage. An experimental setup with an optical fiber inserted in a dilatometer furnace allowed for light emission detection simultaneously to the electric current pulse in zirconia-yttria and also in tin dioxide specimens upon electric field-assisted sintering.

Keywords: Electric field assisted-sintering; Flash sintering; Light emission; Zirconia; Tin dioxide

1. Introduction

Electric field-assisted sintering has been applied to electroceramics since it was recently reported that high density and small average grain sizes might be achieved by applying a dc or ac electric field to polycrystalline yttria-stabilized zirconia solid electrolytes at temperatures lower than that usually required.[1] The technique has been successfully used in several electroceramic materials, mainly oxides.[2–25] Several attempts have been set forth to understand the underlying mechanisms responsible for sintering with or without densification: besides Joule heating, which results from the electric current pulse derived from the application of the electric field, nucleation of defects has been also claimed to induce mass diffusion with consequent sintering.[5] Analysis of what happens when an electric current pulse crosses a polycrystalline sample has been reported by several authors,[17,26] but analysis and experimental evidences on how the electric field produces that electric current pulse are still lacking. Recently it has been pointed out that "there are three things really going on at the same time: electronic conductivity, mass transport and photoemission".[27] However, using three experimental methods, *in situ* atomic emission spectroscopy, direct visual observation, and ultrafast *in situ* voltage measurements, no evidence of plasma generated between particles was found during the spark plasma sintering (SPS) process.[28,29] We must point out that SPS employs low dc fields (few V cm^{-1}) and high currents (usually kA) through a *graphite die* containing the ceramic powder, whereas electric field-assisted sintering employs relatively high fields (100 V cm^{-1}) and low currents (mA–A) through *the specimens*.

Let us consider what happens, from the physical point of view, to a polycrystalline metal oxide pressed pellet under an external electric field. Before that, we have to take into account (i) the electrical behavior of the metal oxide (dielectric, ionic, electronic or mixed conductor), (ii) the temperature (it determines the electrical behavior and the concentration of point defects), (iii) the atmosphere (oxidizing, neutral or reducing) and (iv) the magnitude (might produce dielectric breakdown, bulk and/or surface motion of charge carriers) and the nature of the electric field (dc may polarize and/or transport charge as well mass, ac does not polarize and transports only charge). Moreover, a metal oxide green pellet consists usually of a number of strained particles pressed together. The application of a dc electric field might produce local dielectric breakdown inside the pellet (due to the

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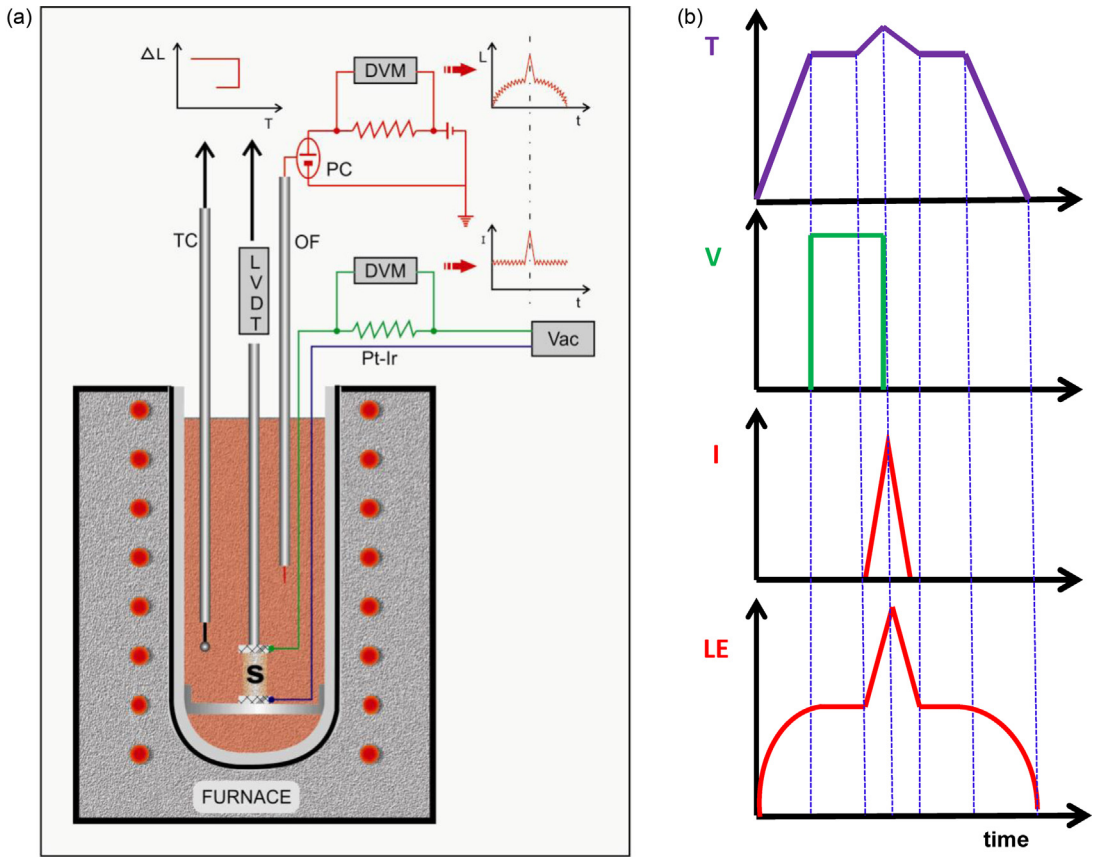

Fig. 1. (a) Experimental setup for simultaneous collection of shrinkage and light emission data from ceramic pellets upon electric field-assisted sintering. S—Sample, TC—thermocouple, LVDT—displacement transducer, OF—Optical fiber, DVM—Digital voltmeter, Vac—ac Power supply, PC—Photocell, I—electric current, t—time, L—Light emission, ΔL—Linear shrinkage. (b) Scheme of temperature, voltage, current and light profile during the electric field-assisted sintering experiment. LE—Light emission.

production of bound charges, which depends on the electric permittivity of the ceramic particles)[30] and electric discharges of the entrapped gas. The required physical conditions, namely, sufficient field strength, availability of gaseous ionic species, and sufficient high local temperatures are met.[27] Under these circumstances, photons might be emitted in the bulk as well as at the surface of the pellets. Now we get to the main objective here: to look for and to detect light emission *during* electric field-assisted sintering of electroceramics, whether it really occurs. Focus has been directed to two different electroceramics: cubic zirconia-yttria (oxide ion conductor) and rutile-tetragonal tin dioxide (electronic semiconductor).

To our knowledge, no experimental evidence had been published on photoemission during electric field-assisted sintering, besides the very recent paper by Lebrun and Raj,[31] where photoemission was detected during the increase in the electrical conductivity of flash-sintered zirconia: 3 mol% Y_2O_3, even in pre-sintered dense specimens. Optical emission spectra were recorded allowing for preliminary identification of the origin of the light pulse during flash sintering. Their explanation, which remains to be confirmed, was that photoemission and electrical conductivity in that ceramic are related to the concentration of electron-hole pairs. The main difference between their results and ours is the following: (a) their experiments allowed for collecting the spectral distribution of the emitted light and ours do not; (b) they carried out experiments only on yttria stabilized zirconia and we detected photoemission in both ionic conducting yttria stabilized zirconia and in electron conducting tin dioxide.

2. Experimental

Cubic ZrO_2: 8 mol% Y_2O_3 ceramic powder from Tosoh, Japan, hereafter 8YSZ, wasused. The powder was pressed uniaxially and isostatically under 46 MPa and 200 MPa, respectively, to ϕ5 mm × 5 mm thick pellets with green relative densities approximately 50%. tin (IV) oxide and manganese (IV) oxide from Alfa Aesar (99%) were used for preparing SnO_2:5 wt.% MnO_2 pellets by thoroughly mixing the stoichiometric amounts of the powders, uniaxially cold-pressing at 30 MPa and isostatically at 200 MPa.

Fig. 1a shows the experimental arrangement for detecting light emission inside the dilatometer furnace. A quartz optical fiber (ϕ3.18 mm, 1 m long) was inserted on a top aperture of the vertical furnace, and for preventing its thermal degradation its sensing tip was fixed down to approximately 15 cm from the sample holder. The light pulse emitted from the top surface of the ceramic sample could reach the optical fiber through the holes of a platinum mesh used as the top electrode. A photoelectric cell with terminal leads connected in series to a V_{dc}–R (3 V–20 k Ω) circuit was positioned on top of the outer tip of

the optical fiber. Two electric signals were collected in a data logger: one from the photocell, due to light emission from the dilatometer furnace being heated and during the electric current pulse through the ceramic specimen; the other from the electric current pulse delivered to the sample. Further details of the complete experimental setup without the optical fiber have been published elsewhere.[20] The experimental sequence for light detection was the following: the electroceramic green pellet was inserted in the dilatometer programmed to heat at 10 °C min^{-1}up to 900 °C with a dwelling time of 5 min and to cool at 10 °C min^{-1} down to 200 °C. During the course of the whole temperature profile, the light emission, mainly due to radiant energy from the heated sample and neighboring furnace components, is detected as a function of time. Subsequently, a similar (same size and compaction procedures) sample was inserted in the dilatometer to follow the same temperature profile as before. When the dilatometer temperature reaches 900 °C, an electric field (usually 100 V cm^{-1}, limiting current 5 Å, with the ability of turning the field off when the dilatometer gauge indicates the occurrence of shrinkage) is applied to the sample. Any light being emitted from the sample would modify the previously recorded light × time profile. Fig. 1b shows a sketch of what is expected to occur during the electric field-assisted sintering experiment. Upon heating, the optical fiber detects the increasing infrared and visible radiation from the environment (sample and dilatometer furnace). When the furnace reaches the dwelling temperature (for the isothermal experiment), the optical fiber light signal is constant up to the time the electric current pulse occurs due to the application of the electric field. At this time, a light pulse is detected simultaneously to the electric current pulse and to an increase in the sample temperature, which decreases as soon as the electric voltage is turned off. For the rest of the experiment the light signal is constant with constant temperature and decreases for decreasing temperature up to the end of the experiment.

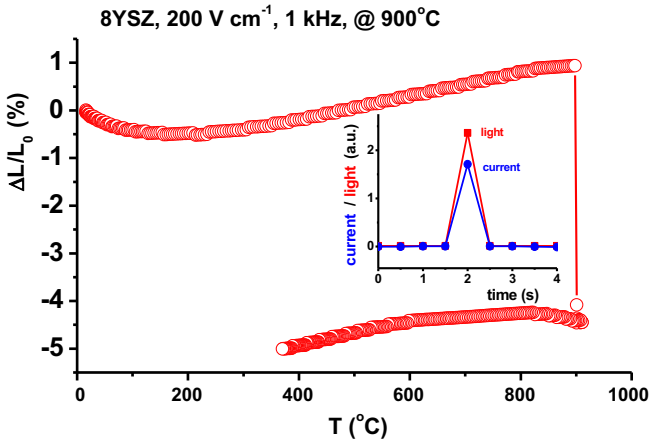

Fig. 2. Dilatometric curve of 8YSZ ceramic upon application of an electric voltage at 900 °C. Inset: Light pulse and electric current pulse at the time of the voltage application.

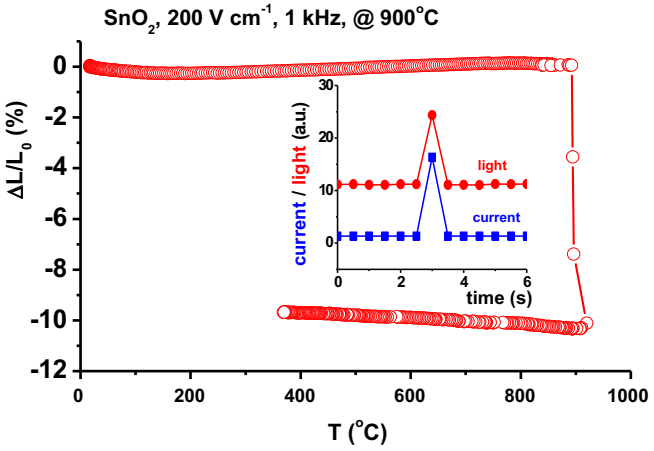

Fig. 3. Dilatometric curve of SnO_2: 5 wt.% MnO_2 ceramic upon application of an electric voltage at 900 °C. Inset: Light pulse and electric current pulse at the time of the voltage application.

3. Results and discussion

Fig. 2 shows the first successful experiment carried out in a ϕ5 mm × 3 mm 8YSZ green pellet heated up to 900 °C and submitted to 60 Vac (1 kHz). At 900 °C a sudden shrinkage of approximately 4.5% is monitored in the dilatometer gauge simultaneous to an electric current pulse of amplitude 1.5 A, a sample temperature increase *and* a light pulse from the photocell (inset). To be certain that this was not an electrical coincidence effect, the power supply for applying the electric voltage and the digital voltmeter for detecting the voltage drop from the electric current of the photocell were connected to independently grounded bench 110 V–60 Hz supplies. Moreover, the experiment was repeated for a SnO_2: 5% MnO_2 green pellet. The result is shown in Fig. 3. Similar photocell current spike is detected when the electric current pulse crosses the sample.

The similarity between both Figs. 2 and 3 with light detection on ZrO_2: 8 mol% Y_2O_3 and SnO_2: 5 wt.% MnO_2 is an evidence that light is emitted from these ceramics during electric field-assisted sintering. Whether that light is due to (i) plasma occurring in gaseous species trapped at pores in the packed particles which constitute the pressed pellets or (ii) electron-hole recombination[31], is a question yet unsolved. One should also take into account that the specimen is expected to get hot at the power spike and at these temperatures it will give out light according to Stefan's law.[1,9,32,33] Further experiments are required to support these assumptions.

4. Conclusions

Light emission has been detected during electric field-assisted sintering of both yttria-stabilized zirconia (ionic conductor) and tin dioxide (electronic conductor) electroceramics, meaning that this is a phenomenon that does not depend on the electrical behavior of the electroceramic. The collected data, light emission simultaneous to electric current pulse and shrinkage, might be an evidence of interparticle gaseous discharge occurring prior to the sintering process.

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